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1987 MMI INTERNATIONAL SYMPOSIUM on

POLYMER MELT DYNAMICS

August 16-19, 1987

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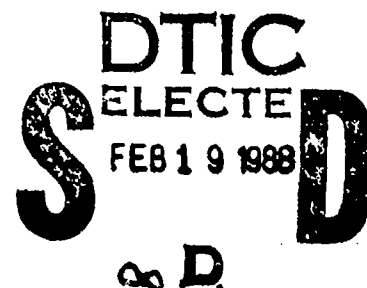
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Final report

MICHIGAN MOLECULAR INSTITUTE

Midland, Michigan

N00014-87-G-0196



ACKNOWLEDGEMENTS:

The Symposium Organizing Committee would like to thank the many scientists who provided suggestions for the program during the planning stages of this symposium. We would also like to express our gratitude to the following organizations for their generous support:

Michigan Polymer Consortium, Midland, Michigan

The Dow Chemical Company, Midland, Michigan

Department of the Navy, Office of Naval Research, Chicago, Illinois

1987 MMI INTERNATIONAL SYMPOSIUM on

POLYMER MELT DYNAMICS

August 16-19, 1987

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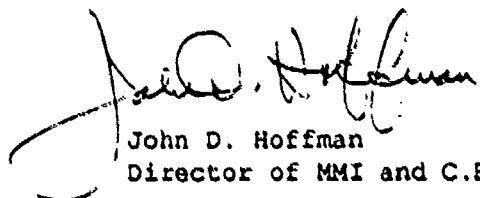
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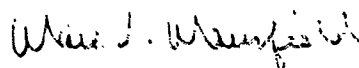
August 16, 1987

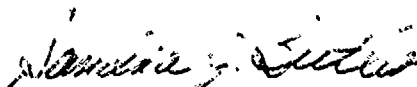
WELCOME TO MMI:

Thank you for your participation in the MMI symposium on "Polymer Melt Dynamics." A special thanks goes to those who have agreed to speak, act as session moderators, provide music for our entertainment, and who have submitted posters.

This year's symposium is the 18th in a series of international symposia sponsored by MMI beginning in 1972. We anticipate a lively and interesting symposium. Please let us know if we can do anything to make your stay in Midland more enjoyable.


John D. Hoffman
Director of MMI and C.E.O


Marc L. Mansfield
Symposium Chairman


Sandra J. Butler
Symposium Secretary

-- TRANSPORTATION SCHEDULE --

<u>DAY</u>	<u>PICK-UP</u>	<u>BUS</u>	<u>LEAVING TIME</u>	<u>DESTINATION</u>
<u>FOR THE HOLIDAY INN REGISTRANTS:</u>				
Sunday	Holiday Inn	Dial-a-Ride	6:45 PM	MMI
	MMI	Dial-a-Ride	9:00 PM	Holiday Inn
Monday	Holiday Inn	Dial-a-Ride	8:30 & 8:45 AM	MCftA*
	MMI	Dial-a-Ride	4:00 & 4:15 PM	Holiday Inn
	Holiday Inn	Dial-a-Ride	5:15 & 5:30 PM	Barstow Woods
	Barstow Woods	Dial-a-Ride	6:45 & 7:00 PM	MCftA
	MCftA	Dial-a-Ride	9:15 & 9:30 PM	Holiday Inn
Tuesday	Holiday Inn	Dial-a-Ride	8:30 & 8:45 AM	MCftA
	MCftA	Dial-a-Ride	4:00 & 4:15 PM	Holiday Inn
	Holiday Inn	Dial-a-Ride	5:00 & 5:15 PM	MCftA
	MCftA	Dial-a-Ride	9:15 & 9:30 PM	Holiday Inn
Wednesday	Holiday Inn	Dial-a-Ride	8:30 & 8:45 AM	MCftA
	MCftA	Dial-a-Ride	1:15 & 1:30 PM	Holiday Inn

FOR THE DAYS INN REGISTRANTS:

Sunday	Days Inn	Dial-a-Ride	6:45 PM	MMI
	MMI	Dial-a-Ride	9:00 PM	Days Inn
Monday	Days Inn	Dial-a-Ride	8:30 & 8:45 AM	MCftA*
	MMI	Dial-a-Ride	4:00 & 4:15 PM	Days Inn
	Days Inn	Dial-a-Ride	5:15 & 5:30 PM	Barstow Woods
	Barstow Woods	Dial-a-Ride	6:45 & 7:00 PM	MCftA
	MCftA	Dial-a-Ride	9:15 & 9:30 PM	Days Inn
Tuesday	Days Inn	Dial-a-Ride	8:30 & 8:45 AM	MCftA
	MCftA	Dial-a-Ride	4:00 & 4:15 PM	Days Inn
	Days Inn	Dial-a-Ride	5:00 & 5:15 PM	MCftA
	MCftA	Dial-a-Ride	9:15 & 9:30 PM	Days Inn
Wednesday	Days Inn	Dial-a-Ride	8:30 & 8:45 AM	MCftA
	MCftA	Dial-a-Ride	1:15 & 1:30 PM	Days Inn

***Midland Center for the Arts**

There will be no charge for the above scheduled bus transportation. PLEASE BE PROMPT FOR ALL BUS PICK-UPS, THEY WILL NOT WAIT LONG.

For other transportation needs call:

Dial-a-Ride (\$1/ride)	631-9011
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CHECK OUT TIMES:

Holiday Inn -- 12:00 noon, you should check-out before coming to the meeting on Wednesday morning. If your flight leaves at a later time you may leave your luggage at the motel. Please check with the front desk on where to store it.

Days Inn -- 12:00 noon, you should check-out before coming to the meeting on Wednesday morning. If your flight leaves at a later time you may leave your luggage at the motel. Please check with the front desk on where to store it.

PROGRAM
SYMPOSIUM XVIII: POLYMER MELT DYNAMICS

Michigan Molecular Institute
August 16-19, 1987

Sunday, 16 August 1987

7:00 PM RECEPTION AND REGISTRATION

MMI

Monday, 17 August 1987

MCftA*

9:00 AM WELCOME

J. D. Hoffman, Director of MMI

SESSION CHAIRMAN:

B. Zimm, University of California, San Diego

9:15 AM

A Generalized Rouse Theory for Entangled Polymer
Liquids (1)

W. Hess, Universitat Konstanz, Federal Republic of Germany

10:15 AM

--Coffee Break--

10:30 AM

Alternative Views of Chain Entanglements (2)

M. Fixman, Colorado State University, Fort Collins, CO

11:30 AM

Long Time Dynamic Properties of Dense Polymer
Model Systems (3)

J. Skolnick, Washington University, St. Louis, MO

12:30 PM

--Lunch--

Garden Room, MCftA

2:00 PM

POSTER SESSION (Wine and Cheese) (14-)
(Tour of new Polymer Technology Center Complex)

MMI

5:30 PM PICNIC IN THE PARK

Barstow Woods

SESSION CHAIRMAN:

C. N. Guttman, National Bureau of Standards

7:15 PM

Polymer Dynamics in Random Fields (4)

M. Muthukumar, University of Massachusetts, Amherst, MA

8:15 PM

Dynamics of Entangled Polymers (5)

M. Rubinstein, Eastman Kodak Company, Rochester, NY

* all of the Lectures will be in the Lecture Hall of the Midland Center for the Arts

Tuesday, 18 August 1987

SESSION CHAIRMAN:

E. Helfand, AT&T Bell Laboratories

9:00 AM What is Reptation? (6)
H. Yu, University of Wisconsin, Madison, WI

10:00 AM --Coffee Break--

10:15 AM Dynamics in Entangled Polymer Blends (7)
J. Klein, Weizmann Institute, Rehovot, Israel

11:15 AM Critical Test of the Dynamics of Entangled
Polymers (8)
R. Wool, University of Illinois, Urbana, IL

12:15 PM -- Lunch-- Garden Room, MCftA

1:30 PM Planned Activities (see attached sheet)
(Posters will also continue to be on
display at MMI for those interested)

5:00 PM SYMPOSIUM BANQUET Garden Room, MCftA

5:00 PM Cocktails

5:45 PM Dinner

6:45 PM Music by Professors Zimm and Stockmayer

SESSION CHAIRMAN:

E. A. DiMarzio, National Bureau of Standards

7:15 PM Many-Chain Interactions in the Reptation Model (9)
J. Deutsch, University of California, Santa Cruz, CA

8:15 PM A Reptation Model with Relaxation Exponent of $10/3$ (10)
N. Shlesinger, Office of Naval Research, Arlington, VA

Wednesday, 19 August 1987

SESSION CHAIRMAN:

W. H. Stockmayer, Dartmouth College

9:00 AM Entanglements and Chain Motion in the Glassy State (11)
J. Bendler, General Electric Company, Schenectady, NY

10:00 AM --Coffee Break--

10:15 AM Dynamics of Polymers in Polydisperse Melts (12)
N. Doi, Tokyo Metropolitan University, Tokyo, Japan

11:15 AM Polymer Melt Dynamics in the Presence of Reversible
Chain Scission (13)
N. Cates, University of California, Santa Barbara, CA

12:15 PM --Lunch-- Garden Room, MCftA

End of Conference

PLANNED ACTIVITIES

for

Tuesday Afternoon

Please sign-up on the Information Board for the activity you wish to participate in. Unless otherwise indicated, there will be no charge for these activities.

Tour of Dow Gardens -- 1:30 PM Host: C. Warner, S. Butler
Meet at the entrance of the Information Building located on the south side of the Center for the Arts.

Golfing at Curry Golf Course -- 1:30 PM Host: M. Shoemaker, M. Bauer
Golf clubs may be rented at the course for \$2.50/9 holes.
Meet at the West St. Andrews side of the Center for the Arts (north).

Tennis -- 1:30 PM Host: S. Dent, M. Mowery
Courts are available at several different sites in Midland, if you do not have a tennis racquet, please see S. Butler by Monday noon, she will try to arrange one for you. Meet in front of MNI.

Swimming on Sanford Lake -- 1:30 PM Host: W. Brumwell, K. Battjes, K. Dunker
Please bring your own suit and towel. Meet at the West St. Andrews side of the Center for the Arts (north).

A T T E N D E E S

POLYMER MELT DYNAMICS

August 16-19, 1987

Michigan Molecular Institute

PRE-REGISTERED ATTENDEES

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Madison, WI 53706

Bruno R. Zimm
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(San Diego)
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A B S T R A C T S

→ This symposium described
information concerning;

Monday, August 17, 1987, 9:15 AM

✓
A GENERALIZED ROUSE THEORY FOR ENTANGLED POLYMERIC LIQUIDS

Walter Hess, Universität Konstanz and Max-Planck-

Institut für Polymerforschung

Starting from the Liouville equation for a system of interacting chains, relaxation equations for the segment coordinates of one test chain are derived. These equations have the form of generalized Rouse equations with a time-dependent memory kernel instead of a constant relaxation time. The memory kernel can be related to a dynamic friction function, which is given by the correlation function of forces between test chains and the other chains of the system. A systematic calculation of the friction function is proposed, which relies on the translational invariance of the interaction potential of two chains against curvilinear displacements¹. This symmetric principle is only violated by the end effects of the chains. To zero order in the end effects curvilinear motion and lateral motion are decoupled, curvilinear motion is unhindered motion of a one-dimensional Rouse chain, lateral motion is strongly hindered by interaction and freezes in at a critical chain length or concentration. This might be called the reptation transition. The friction function is now calculated to first order in the end effects (using the zero-order curvilinear and lateral propagators). Beyond the reptation transition the spectrum splits into high-frequency Rouse modes and into a low-frequency part, which is dominated by interaction effects. As an example the tracer diffusion coefficient is treated. In the long-chain limit D_t can be written as $D_t = D_R + D_{C.R.}$. Whereas the reptation term agrees with the result of the phenomenological theories, $D_R \sim n_t^{-2}$, I find that the constraint release mechanism is much stronger than in the phenomenological theories. The result is $D_{C.R.} \sim n_t^{-1} n_p^{-1}$, when n_t , n_p are polymerization degrees of tracer and matrix polymers, respectively.

1) W. Hess, Macromolecules 19, (1986) p. 1395

Monday, August 17, 1987, 10:30 AM

200-168
ALTERNATIVE VIEWS OF CHAIN ENTANGLEMENTS ;

Marshall Fixman, Colorado State University

Three aspects of the motion of rod and chain polymers in the semidilute and concentrated regimes will be discussed: (1) The failure of dynamical simulations to show visible evidence for reptative motion in tubes. (2) The propensity of experiments and simulations to show that the longest relaxation time τ_1 for angular rotation or internal stresses is greater than the time τ_t for a molecule to diffuse across one radius of gyration ($\tau_1 \sim N^{3.4}$ and $\tau_t \sim N^3$, where N is the chain length). (3) The quantitative description of models devised on the assumption that these observations are not misleading and would persist to arbitrarily large chain length.

Monday, August 17, 1987, 11:30 AM

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LONG TIME DYNAMIC PROPERTIES OF DENSE
POLYMER MODEL SYSTEMS

Jeffrey Skolnick, Washington University

Dynamic Monte Carlo simulations of long chains confined to a cubic lattice at a polymer volume fraction of $\phi = 0.5$ were performed to investigate the dynamics of polymer melts. In the range of chain lengths n , from $n = 64$ to $n = 800$, this model system exhibits a crossover from a weaker dependence of the diffusion coefficient D on chain length to a much stronger one, consistent with $D \sim n^{-2}$. Since the n^{-2} scaling relation signals the onset of highly constrained dynamics, an analysis of the character of the chain contour motion was performed. In agreement with previous simulations on a diamond lattice, no evidence for the well-defined tube required by the reptation model of polymer melt dynamics was found. The lateral motions of the chain contour are still large even in the case when $n = 800$, and the motion of the chain is essentially isotropic in the local coordinates. Hence, the crossover to the $D \sim n^{-2}$ regime with increasing chain length of this monodisperse, model melt is not accompanied by the onset of reptation dynamics.

We then explored the dynamics of a probe chain consisting of $n_p = 100$ segments in a matrix of chains of length of $n_M = 50$ up to $n_M = 800$ at a total volume fraction of polymer $\phi = 0.5$. Since the diffusion constants of a melt with $n = 100$ and 800 differ by two orders of magnitude, an essential assumption of reptation theory that there is a separation of time scales between the probe and matrix motion holds; perhaps, in this system, the probe chains might reptate. The diffusion coefficient of the probe chain over the range of n_M under consideration decreases by about 30%, a behavior rather similar to that seen in real melts of very long chains. However, the analysis of the probe chain motion shows that the mechanism of motion is not reptation-like and that the cage effect of the matrix is negligible. That is, the local fluctuations of the topological constraints imposed by the long matrix chains (even for $n_M = 800$) are sufficiently large to provide for essentially isotropic, but somewhat slowed down, motion of the probe chains relative to the homopolymeric melt. The results of these MC experiments are discussed in the context of theoretical predictions and experimental findings for related systems.

Monday, August 17, 1987, 7:15 PM

POLYMER DYNAMICS IN RANDOM FIELDS

M. Muthukumar, University of Massachusetts

Dynamic and static properties of a polymer chain with and without self-excluded volume, which performs Brownian motion between randomly distributed impenetrable fixed obstacles, have been investigated by Monte Carlo simulations and analysed by scaling and theoretical considerations. The mean square radius of gyration, $\langle S^2 \rangle$, the center of mass diffusion coefficient D and the longest relaxation time τ are functions of $x = (1-p)\sqrt{N}$ for all chain lengths N and porosities p above the percolation threshold. Simulations have been performed for $x \leq 10$.

With increasing x the radius of gyration of a Gaussian chain exhibits a crossover from Gaussian statistics $\langle S^2 \rangle \sim N$ to a collapsed state where $\langle S^2 \rangle$ is independent of N . This phenomenon is attributed to the effects of both the lack of self-excluded volume and the presence of an effective self-attractive potential arising from random repulsion between polymer and the solid particles of the medium and is analysed using the "replica trick."

We do not observe reptation in our simulations although the system simulated here is the birthplace of reptation. The strong dependency upon chain length of $D \sim N^{2.9 \pm 0.3}$ and $\tau \sim N^{4.0 \pm 0.4}$ is conjectured to result from randomly distributed bottle-necks and traps in the porous solid. If these local constraints are released by arranging the obstacles in a periodic array, familiar reptation dynamics and $\langle S^2 \rangle \sim N$ are observed. An effective medium theory which is analogous to that of Edwards and Grant has been derived for the current problem which is in good agreement with our Monte Carlo results. Our simulations do not show reptation even if the excluded volume effect is present for the chain.

Monday, August 17, 1987, 8:15 PM

DYNAMICS OF ENTANGLED POLYMERS

Michael Rubinstein, Eastman Kodak Company

In the first part of the talk the idea of a confining tube is reexamined and a new definition of an entanglement net is suggested. The second part deals with dynamics of a single chain in an array of fixed obstacles. The "repton" model incorporating reptation and fluctuations in tube length is proposed and solved. In the third part the many chain effects, called constraint release, are self-consistently included in the theory and the predictions are compared with oscillatory shear data of binary blends. In the last part the dynamics of non-linear entangled polymers, such as stars, rings, etc. are discussed.

Tuesday, August 18, 1987, 9:00 AM

WHAT IS REPTATION?

Hyuk Yu, University of Wisconsin

This is to focus on the experimental studies of polymer translational diffusion relative to the reptation model. Despite the much heralded agreement with the model prediction for the molecular weight dependence of polymer self diffusion in bulk, $D_s \propto M^{-2}$, detailed experimental studies of various polymers in different media have started to highlight lack of stringency of the commonly accepted reptation criterion, namely $D_s \propto M^{-2}$. The paper will review the current status of chain diffusion studies whereby conformity and discordance with the above criterion will be examined critically. Discussion will center around a proposition that the reptation mechanism is yet to be established universally by experiment as the dominant mode for chain translation diffusion, notwithstanding the initial euphoria that has swept through the community.

Tuesday, August 18, 1987, 10:15 AM

DYNAMICS IN ENTANGLED POLYMER BLENDS

Jacob Klein, Weizmann Institute of Science

Infra-red microdensitometry, X-ray microanalysis with electron microscopy, and Rutherford backscattering methods are being used to study mutual diffusion in a variety of compatible and partly compatible binary polymer blends. In the compatible blend poly(vinyl chloride) (PVC) / poly(caprolactone) (PCL) the mutual diffusion coefficient $D(\phi)$ has a strong maximum near the 50/50 blend composition ($\phi = 0.5$); this leads to highly non-fickian concentration profiles on interpenetration between the two pure bulk polymers - which are quantitatively consistent with the independently determined form of $D(\phi)$.

For a blend of long and short (but highly entangled) chains of a homopolymer, both of which are reptating, our results show that the mutual interpenetration is controlled by the mobility of the shorter chains, shedding light on a recent controversy in the literature. Finally, we measured the diffusion broadening with time of an originally sharp interface between two compatible polymers (with a lower critical solution temperature) at temperatures on both sides of the critical temperature: the results show clearly the fall in the mutual diffusion rate at the higher temperatures, where the system is in the two-phase region.

The collaboration of R.A.L. Jones, E.A. Jordan, J. Sokolov, M. Rafailovich, S.A. Rocca, L.J. Fetters and A.M. Donald is gratefully acknowledged, as is donation of polymers by J. Higgins, P. Tomlins and H. Fruitwallah for some of the studies.

Tuesday, August 18, 1987, 11:15 AM

CRITICAL TESTS OF THE DYNAMICS OF ENTANGLED POLYMERS

Richard P. Wool, University of Illinois

Tests of reptation models for the molecular dynamics of polymer melts were conducted by FTIR analyses of selectively deuterated polystyrene (PS) melts, computer simulation and other techniques. Some important results are as follows: (1) FTIR dichroism studies of step-strained centrally deuterated symmetric triblock PS melts (115 C) demonstrate that relaxation of the protonated chain ends first occurs while the deuterated center retains its orientation. The central part of the chain then relaxes at a rate predicted by tube models. This result provides strong support for the tube evaporation mechanism of reptation. (2) Relaxation rates of deuterated chains, M , in protonated matrices of molecular weight, P , indicated that the relaxation rate, T , behaved as $T \propto P^{1.2} M^2$ for $P \ll M$ and that $T \propto P^0 M^3$ for $P > M$. This result is in agreement with our computer simulation studies and supports the constraint release mechanism but differs with the chain-end fluctuation theory and with some results from tracer diffusion experiments. (3) Correlated motion for monomer diffusion at times less than the reptation time, T_r , is being explored using Sputtered Neutral Atom Mass Spectrometry (SNMS) studies of PS interfaces. The critical prediction to test from reptation theory is that the number of monomers interdiffused, N , behaves as $N \propto t^{3/4} M^{-1/4}$ for $t < T_r$. (4) The fractal nature of diffusion and potential connectivity factors affecting the zero-shear viscosity will be discussed with these results.

Tuesday, August 18, 1987, 7:15 PM

MANY-CHAIN INTERACTIONS IN THE REPTATION MODEL

Joshua M. Deutsch, University of California, Santa Cruz

Theoretical and numerical work is presented extending the reptation model to include many chain interactions. The relaxation time for long chains is argued to scale as $\exp(\text{const. } M^{2/3})$ where M is the molecular weight. A lattice simulation using reptation dynamics also confirms this prediction. The dynamics of rings will also be discussed.

Tuesday, August 18, 1987, 8:15 PM

A REPTATION MODEL WITH RELAXATION EXPONENT OF 10/3

Michael F. Shlesinger, Office of Naval Research

The reptation model of DeGennes was introduced to determine diffusion and flow properties of long entangled polymers in a melt. A single chain calculation led to the reptation time τ varying with the chain mass as M^3 . Scher and Shlesinger proposed a multichain framework which predicted τ varying as M^x with $3 < x \leq 3.5$, and demonstrated that this is compatible with the theoretical and experimental determination of the M^{-2} behavior of a chain's diffusion constant. The present work finds $x = 10/3$ which finally brings the reptation concept into agreement with experiments.

Wednesday, August 19, 1987, 9:00 AM

→ ENTANGLEMENTS AND CHAIN MOTION IN THE GLASSY STATE

John T. Bendler, General Electric Company

A series of mechanical and optical studies have been carried out on carefully-prepared (isotropic) samples of bis-phenol A polycarbonate in the glass state to determine the influence of strain, temperature and thermal history on the solid state behavior. (1) Stress relaxation, creep, birefringence/strain recovery, and stress-strain response are rationalized using a simple network model of the glass. Both anelastic and plastic strain accompanies deformation. The former is interpreted in terms of conformational equilibration between entanglement points via mobile-defect migration along and between network segments. Plastic flow can result from defect loss at dangling ends. Entanglement motion (or movement of chain density past junction points) does not occur, in contrast to the melt above T_g . Conformational motions in polycarbonate are described to explain the constitutive model and observed kinetics.

1. D.G. LeGrand, W.V. Olszewski and J.T. Bendler, J. Polym. Sci. Polym. Phys. Ed. 25, 1152 (1987).

Wednesday, August 19, 1987, 10:15 AM

→ DYNAMICS OF POLYMERS IN POLYDISPERSE MELTS . ←

Masao Doi, Tokyo Metropolitan University

The dynamic behavior of a mixture of two homopolymers with narrow molecular weight distribution is analyzed on the basis of the concepts of reptation and constraint release. We propose that constraint release causes not only the tube renewal (the relaxation of the tube), but also tube dilation (the enlargement of the effective tube diameter). A general scheme of accounting for these effects is given. The diffusion constants and the relaxation modulus of the mixture is predicted as a function of the molecular weight of each component and their mixing ratio.

Wednesday, August 19, 1967, 11:15 AM

POLYMER MELT DYNAMICS IN THE PRESENCE OF
REVERSIBLE CHAIN SCISSION REACTIONS

Michael E. Cates, University of California, Santa Barbara

Within the framework of the tube model, a theory is presented of stress relaxation in systems of concentrated polymers that can undergo reversible chain-scission reactions on experimental time scales. The model should be relevant to the description of flexible surfactant micelles, end-linking functionalized polymers, and equilibrium polymers such as liquid sulfur at high temperatures. When the average time τ_{break} for a chain to break into two pieces is shorter than τ_{rep} (the reptation time of an unbroken chain), the terminal time, τ , for stress relaxation is determined by a new mechanism involving a co-operation between scission and chain diffusion. As a result, τ varies with fractional powers of the monomeric friction factor and the reaction rate constants. The model provides a good account of the magnitude and temperature dependence of the viscosity of liquid sulfur; this viscosity is roughly five orders of magnitude less than would be the case if reptation alone was the dominant relaxation mechanism.

DYNAMICS OF STYRENE-ISOPRENE-STYRENE TRIBLOCK COPOLYMERS
SYSTEMS CONTAINING SMALL AMOUNTS OF DIBLOCK
AND HOMOPOLYMER MOLECULES

Charles A. Berglund, The Dow Chemical Company

Triblock copolymers with polystyrene endblocks (15%) and polyisoprene midblocks form elastomers at temperatures between the glass transitions of the blocks due to pseudo-crosslinking by the dispersed polystyrene domains. These systems are rarely composed entirely of perfect triblock molecules, however, and the viscoelastic properties are influenced by the presence of small amounts of other molecules which are, or can behave as, either a diblock or homopolymer. The effects of these species can be explained using the concepts of reptation and constraint release. Both homopolymer and diblock are found to contribute to dynamic mechanical loss in the rubbery plateau for isochronal data. The homopolymer relaxes at a lower temperature than the diblock since it is free to reptate while the diblock must relax by constraint release. Stress relaxation data indicate that relaxation from the rubbery plateau in these systems occurs by a two step process, probably involving endblock diffusion out of polystyrene domains and reptation of the entire chain through the matrix. The stress relaxation modulus shows an additional plateau region, at times longer than those corresponding to the rubbery plateau, before $G(t)$ decreases sharply as the system apparently undergoes flow. The two step process also results in a maximum in tangent delta as a function of frequency at 150C. The maximum is moved to higher frequency by the addition of polyisoprene homopolymer, which enhances the constraint release mechanism. Increasing molecular weight increases the reptational relaxation time and shifts the maximum to lower frequency.

NORMAL MODE ANALYSIS OF LATTICE MODEL POLYMER CHAINS
AT HIGH CONCENTRATIONS

Charles C. Crabb*, David F. Hoffman, Michelle Dial
and Jeffrey Kovac, University of Tennessee

The dynamic behavior of simple-cubic and face-centered-cubic lattice model polymer chains was simulated using a Monte Carlo method. The chain relaxation was analyzed using the Rouse normal coordinates. We find that normal mode analysis accurately describes chain relaxation at all concentrations studied. No cross-correlations are observed between modes. The chain length dependence on the relaxation times is found to be a function of both concentration and mode number. Some differences between lattices are also observed.

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REPTATION IN ANISOTROPIC MEDIA

William W. Merrill and Matthew Tirrell, University of Minnesota

The effect of orientation on simple reptation (ie, neglecting tube length fluctuations and constraint release) has been investigated. Specifically, tube segments created at time t' after a step strain at time zero are no longer isotropically oriented as per Doi and Edwards but rather are oriented to an extent α of the mean orientation in the sample existing at t' . The change in the initial Hermans orientation function $G(0)$ with initial strain has been assumed known, thus only the change in the shape and scale of the time relaxation spectrum is addressed by this study. The decay of the Hermans orientation function $G(t)$ in the terminal zone for chains reptating according to this model has been determined analytically in the case of proportional coupling. This solution provides an upper and lower bound for $G(t)$ in the case of coupling decreasing with decreasing $G(t)$. This more complicated case has been solved for numerically using finite elements. Although the molecular weight power laws for η_0 and $J_e G_N$ are shown to be unchanged by this coupling, the longest orientational relaxation time is found to be substantially greater than the tube lifetime (reptation time) when coupling is significant ($\alpha \sim 0.3$) leading to a discrepancy between the actual tube lifetime and the apparent lifetime measured by (visco-elastic) relaxation experiments. Furthermore, the nonlinear coupling is shown to reduce shear thinning at higher strain rates. Finally, it is shown how pre-orientation may enhance polymer-polymer welding.

DIFFUSION OF BRANCHED AND LINEAR POLYMERS
IN CONCENTRATED SOLUTIONS

Timothy P. Lodge, University of Minnesota

The mechanisms of motion available to macromolecules in concentrated systems are of fundamental importance to synthesis, processing, application, and molecular characterization. The technique of dynamic light scattering from isorefractive ternary solutions permits precise measurement of translational diffusion coefficients for trace amounts of a probe polymer in solution. The variables of interest include the molecular weight and chain architecture of the probe, and the concentration and molecular weight of the "invisible" surrounding matrix chains. Results will be presented for the diffusion of linear, 3-arm star, and 12-arm star polystyrenes in solutions of poly(vinyl methyl ether)/o-fluorotoluene. In general, the results suggest that the postulate of reptation, the snake-like wriggling of linear chains along their own contour length, may not be as directly applicable in solution as it appears to be in the melt. The influence of polymer-polymer thermodynamic interactions on the polystyrene mobility will also be discussed.

**"CO-MO-MODEL", A MODEL OF COOPERATIVE MOTIONS
IN DENSE POLYMER SYSTEMS**

T. Pakula and S. Geyler, Max-Planck-Institut für Polymerforschung

A microscopic model of cooperative motions in condensed polymer systems is presented. The mechanism assumed consists in collective replacements of molecular subsegments within closed loops of motion. The model is applied to computer simulation of polymer chain motions on a lattice with all sites occupied. Results related to static properties and to self diffusion of linear and cyclic chains are reported. Monodisperse systems with chains of various lengths (up to 512 monomer units) have been considered.

It is shown that in equilibrated amorphous dense systems linear chains satisfy the gaussian statistics contrary to cyclic chains which seem to be slightly more collapsed than the gaussian statistics for ring molecules predicts.

Molecular weight dependence of center-of-mass diffusion of linear chains shows a smooth cross-over between $D \sim N^{-1}$ and $D \sim N^{-2}$ dependences observed for short and long chains respectively. The ratio of self diffusion constants of linear and ring chains decreases with chain length reaching values close to 2 for long chains. Stretched exponential relaxation behaviour of the end-to-end vector of linear chains is observed with parameters being chain length dependent (e.g. $\langle t \rangle \sim N^{3.4}$ for long chains).

Reference: T. Pakula, *Macromolecules* 20 (1987) 679.

DYNAMICS OF REVERSIBLY CROSSLINKED CHAINS

L.G. Baxandall, Cavendish Laboratory, Cambridge

The dynamics and linear viscoelastic response of a polymer chain bound by reversible crosslinks to a (phantom) network are considered in a mean field picture. Reversible crosslinks are viewed as entities which whilst intact fix a segment of polymer in space but which spontaneously break and reform to allow the point of attachment and hence the polymer to move. Particular results for small numbers (2, 3 and 4), as a model for ionomer gels, and for large numbers of crosslinks, comparing with Rouse chain dynamics, are given.

ENTANGLEMENT IN BLENDS OF MONODISPERSE STAR AND LINEAR POLYSTYRENES

Hiroshi Watanabe*, Hirotsugu Yoshida, and Tadao Kotaka,
Osaka University, *current address: University of Minnesota

Viscoelastic properties of binary blends of low and high molecular weight monodisperse polystyrenes (designated as 1- and 2-chains, respectively) were investigated. Linear polystyrenes (PS) were used as the 1-chain (with molecular weight M_1), and star and/or linear PS were used as the 2-chain (with molecular weights M_2). In the dilute blends examined, the content w_2 of the 2-chain was kept small so that only the entanglement between the 1- and 2-chains (1-2 entanglement) affected the relaxation of the 2-chain. If M_1 was larger than the characteristic molecular weight M_C but still sufficiently smaller than M_2 , the 2-chain in the blend relaxed in the long time region by the retarded Rouse-Ham-like mode: The compliance of the 2-chain was close to the prediction of the Rouse-Ham theory, and the relaxation time was proportional to $M_1^3 M_2^2$. However, the ratio of the relaxation times of the star and linear 2-chains appeared to be somewhat smaller than that expected from the Rouse-Ham theory, suggesting that the dynamics of the 2-chain in the blends with $M_2 \gg M_1 > M_C$ might not be completely the same as the Rouse-Ham dynamics. The M_2/M_1 ratio necessary for the power-law ($M_1^3 M_2^2$) dependence of the relaxation time to be observed was smaller for the star 2-chain than for the linear 2-chain, presumably because the relaxation modes in the monodisperse system are slower and the competing Rouse-Ham-like mode is realized more easily for the star 2-chain than for the linear 2-chain having the same M_2 . These results suggest that the 2-chain in the dilute blends with $M_2 \gg M_1 > M_C$ relaxes as the surrounding 1-chains diffuse away and 1-2 entanglement becomes ineffective. In the framework of the generalized tube model, this relaxation mode corresponds to tube renewal.

H-POLYMERS IN THE MELT

T.C.B. McLeish, University of Cambridge

The tube model of polymer melts has been successfully applied to linear and star-shaped polymers. It is interesting to extend the approach to the case of H-shaped polymers because these are the simplest that contain polymer chain between branch points. This has important molecular and rheological consequences, which will be presented. Particularly interesting is the response in extensional deformation, which is related to the behaviour of branched polyethylenes in converging flow.

UNITING REPTATION THEORY WITH ENTANGLEMENT NETWORK MODELS
TO DESCRIBE THE MELT DYNAMICS OF LINEAR POLYMERS

Bernard J. Meister, The Dow Chemical Company

A rheological model is proposed for describing the melt dynamics of linear polymers. This is an entanglement model where entanglements are assumed to be formed by reptation. Entanglements are removed by both normal diffusional reptation and by forced reptation in a deformational field. Constraint release is handled by calculating the probability of a given chain end being the shortest chain end and therefore the reptational segment at the entanglement junction. This is similar to the Graessley approach except that each entanglement along the chain is considered for its constraint release capabilities. Predictions of the zero shear viscosity and steady state compliance of blends of monodisperse polymers are closer to published data than any previous models. No constants are introduced to fit the data beyond the monomeric friction coefficient, entanglement length, and measured time-temperature shift factors which all cancel out in comparison with the blend data.

As the deformation rate is increased, the state of entanglement is decreased due to increased forced reptation. Predictions of the viscosity-shear rate curves agree with data on monodisperse, two component blends, and commercial polydisperse polymers. Predictions are also obtained for the relaxation time spectra, primary normal stress coefficient and melt modulus as a function of shear rate.

In contrast to the Doi-Edwards and Curtiss-Bird models, this model is a reptational description of the memory function that can be incorporated in the Lodge formalism for temporary entanglement networks as the entanglement junctions are assumed to follow an affine deformation.

There is much new material in this poster beyond what was presented at the Society of Rheology.

THE MOBILITY OF A REPTATING CHAIN INCREASES WITH STRETCHING

Bruno H. Zimm, University of California, San Diego

When a steady force is uniformly applied to all segments of a reptating chain, the chain moves in response. We have a computer simulation that shows that the speed of this motion, measured as the velocity of the center of mass, increases if the chain is first stretched by another force applied to the ends. This can be understood as a simple consequence of the following argument. In reptation the probe chain is tied to the "primitive path" by the surrounding chains, many of which occur in pairs close together on opposite sides of the primitive path, like the gates of a slalom ski course. Between these gates the probe chain is much more free to spread out in coils away from the primitive path. When the uniform force is applied, the parts of the probe chain that move most efficiently along the path are those parts that lie in the gates; the rest of the chain dissipates the applied force mostly by pushing against the surrounding chains without moving efficiently along the path. If the chain is stretched by another force at the ends, the primitive path is also stretched and acquires more gates. Thus the fraction of the probe chain that lies in the gates and that moves efficiently is increased, and the average motion along the path is speeded up. We suggest that this process is involved in the well known decrease of viscosity with orientation in polymer melts.

PHOTON CORRELATION SPECTROSCOPY FROM DILUTE

POLYMER-POLYMER MIXTURES

Melia Rodrigo* and Claude Cohen, Cornell University

We examine the molecular weight, concentration, and temperature dependences of the initial decay of the light scattering photon correlation from dilute mixtures of polystyrene in polymethylphenyl siloxane. We observe the q^2 -dependence previously reported on these mixtures. For polystyrene molecular weights substantially larger than the polymethylphenyl siloxane matrix, the infinite dilution limit of the diffusion coefficient extracted from the initial decay appears to follow a molecular weight dependence close to $M^{0.5}$. For the very dilute mixtures studied, the thermodynamic interaction effect is very small and the changes in the diffusion appears to due to the effects of concentration on the friction coefficient. The temperature dependence of the initial decay rate of the correlation deviates from an Arrhenius behavior as the coexistence curve of the mixture is approached.

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EXPERIMENTAL EVIDENCES OF RELAXATION PROCESSES
OF THE DOI-EDWARDS MODEL AND FURTHER PROBLEMS

Jean Francois Tassin and Lucien Monnerie,
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The relaxation of the average orientation of stretched polystyrene chains has been studied by infrared dichroism over a large time domain for different narrow distribution samples of different molecular weights.

The behavior at short times appears to be independent of the molecular weight and has been attributed to the local relaxation process between entanglements. The behavior at longer times exhibits molecular weight effects and can be interpreted by the retraction and reptation motions of the Doi-Edwards theory. The existence of these relaxation processes has become more apparent through the study of the relaxation of a chain segment as a function of its location along the chain using isotopically labeled block copolymers. A more rapid relaxation of chain ends has been experimentally observed and accounted for by considering the retraction and reptation processes. As chain length increases, chain ends begin to reptate in a more and more anisotropic medium. Experiments show that, in this case, reptating chain ends do not seem to completely lose their orientation as expected by the model. A phenomenological treatment has been proposed where the orientation of a part of chain leaving the initial tube is assumed to be proportional to the anisotropy of the surroundings.

MOLECULAR REPTATION FROM THE MELT TO A GROWING CRYSTAL FACE OF PE

Rade Ognjanovic and James N. Hay, Cornell University

We studied the effect of molecular weight, branch concentration, branch type and branch sequence distribution of linear low density PE crystallization kinetics. Suitable fractions of PE were obtained by temperature rising elution fractionation and gel permeation chromatography techniques. Differential scanning calorimetry and polarised light microscopy were then used to follow the growth of spherulites and the crystallization kinetics. The crystallization kinetics models of Avrami, Evans and Hoffman were applied to the data and effects due to the four molecular morphologies above were noted.

Molecular weight PE crystallization were governed by viscosity and thermodynamic processes as the chain length was changed. At high molecular weights viscosity tended to show crystallization while thermodynamic considerations would increase crystallization rates.

Branch type Large side branches (isobutyl) hindered crystallization by increasing melt viscosity and/or by acting on the active crystal site at which reptation was occurring.

Branch concentration (the number of side branches per 1000 C atoms of PE chain) High branch densities hindered the crystallization rate. Crystallization can be considered to have an order of crystallization rate similar, in a way, to the order of a chemical reaction. The Avrami n value parameter corresponds to the growth freedom or dimensionality of growth of a growing crystal. The growth freedom decreased with an increase in branch concentration for ethyl branched PE fraction while the large isobutyl branches gave a consistently low value of growth freedom at all the branch concentrations studied.

Branch sequence ^{13}C NMR Markoffian branch sequence distribution statistics divided the fractions into material with branches distributed randomly and those with branch clusters in the chain. Optical growth rate and dsc data did not correlate for the clustered fraction due to the isobutyl blocks "holding off" crystallisable blocks of PE from the growing crystal surface, a mechanism not accounted for in the crystallization models used here. Induction times were recorded (the time from which the sample reached the crystallization temperature from the melt to the time when crystallization began) which increased with the length/number of clusters.

KINETICS OF FORMATION OF THE DIFFUSE INTERFACE BETWEEN
PARTIALLY COMPATIBLE POLYMERS

M. Rafailovitch, J. Sokolov, G. Krausch, R. Mills, R.A.L. Jones and J. Klein,
Cornell University

Rutherford Backscattering was used to measure the concentration profiles between solution chlorinated polyethylene (SCPE) and polymethyl methacrylate (PMMA) after annealing at various temperatures in both the one phase region and the two phase region of the phase diagram. A diffuse interface was observed in both regions of the phase diagram: its width could be characterized by a diffusion coefficient like parameter, whose temperature dependence has a maximum at a temperature markedly above the lower critical solution temperature of the blend. In the one phase region this parameter is simply interpreted in terms of the (concentration dependent) mutual diffusion coefficient of the blend; above the LCST it reflects not only diffusion in the miscible region but also the approach to the equilibrium interface thickness between the two immiscible phases.

A LOOP MODEL OF ENTANGLEMENT IN THE MELT

A. MacArthur and D. McIntyre, University of Akron

Entanglement in high molecular weight polymers is considered both experimentally and theoretically. Thus polymer entanglements are viewed as topological interactions of strands not involving their ends, or loop interactions. Both static and dynamic models have been developed and are applied to experiments on isolated polymer chains and polymer melts.

A scheme for analyzing tangle projections has been developed and leads to (1) an ability to determine the type of entanglement in computer walks, (2) sufficient conditions on the crossing list for tieability, (3) an interaction matrix that rationalizes "blobs", and (4) an alternative method for analyzing knots in general that provides insight into the structure of known knots.

A dynamic equilibrium interpretation involves the rank of the loop interactions and rationalizes the 3.4 power law. A transition probability matrix for the system can be set up that governs the rate at which the system responds to the stress. The relaxation effects after stressing to a new equilibrium state can be obtained by identification of "zero-rank" loops with the earlier Green and Tobolsky calculation of bond breaking in crosslinked systems.

Applications of the model are made with a reinterpretation of previously reported and new experiments on high molecular weight systems. These experiments involve strain birefringence, strain crystallization, die swell, polymer welding, multi-state crosslinking, and membrane viscometry. In particular the effect of small amounts of "increased loop entanglements" is shown to be extremely important to the above properties -- akin to a "gel point" in crosslinking reactions.

ULTRASONIC CHARACTERIZATION OF POLYSTYRENE AS
A FUNCTION OF TEMPERATURE AND PRESSURE

L. Piché and F. Massines,
Industrial Materials Research Institute

We study the propagation of 3 MHz ultrasonic waves in polystyrene. The specific volume (V) is measured together with the velocity (v) and the attenuation (a) of shear and longitudinal waves, in the temperature range from -150°C to 200°C at pressures extending to 1Kbar. These measurements are translated in terms of storage (M') and loss (M'') moduli (longitudinal and shear). For all values of pressure, the general behavior of measurements made as a function of temperature is similar. The specific volume curve allows to define the glass transition zone. We name T_g the beginning of this zone and T_e , the end. Ultrasonic results can be described as follows. On increasing temperature, until T_g we observed an elastic behavior. But, at T_g the attenuation (and M'') suddenly increases and an abrupt change in the slope of the velocity (and M') occurs. At temperature higher than T_e , the velocity and (M') describes a sigmoid type curve and the attenuation (M'') rapidly goes through a sharp maximum before decreasing. An increase in pressure causes the maximum to shift to higher temperature. The observed temperature shift being the same for the specific volume, the velocity, the attenuation and the corresponding moduli, it is suggested that these behaviors have common origin, namely, the glass transition. The results are discussed in terms of the possible application of ultrasonic technique for the characterization of polymers transitions and properties evolution.